(19) World Intellectual Property Organization International Bureau



| 1811 | 11 | 181 | 181 | 181 | 181 | 181 | 181 | 181 | 181 | 181 | 181 | 181 | 181 | 181 | 181 | 181 | 181 |

(43) International Publication Date 18 April 2002 (18.04.2002)

PCT

(10) International Publication Number WO 02/31051 A1

- (51) International Patent Classification⁷: C08L 31/04, 33/08, 33/10, C08K 3/04, H01B 1/06, 9/02, 3/18, 3/42, 3/44
- (21) International Application Number: PCT/US01/31791
- (22) International Filing Date: 11 October 2001 (11.10.2001)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

09/685,574

11 October 2000 (11.10.2000) US

- (71) Applicant: GENERAL CABLE TECHNOLOGIES CORPORATION [US/US]; 4 Tesseneer Drive, Highland Heights, KY 41076 (US).
- (72) Inventor: EASTER, Mark, R.; 4028 North Pennsylvania, Indianapolis, IN 46205 (US).

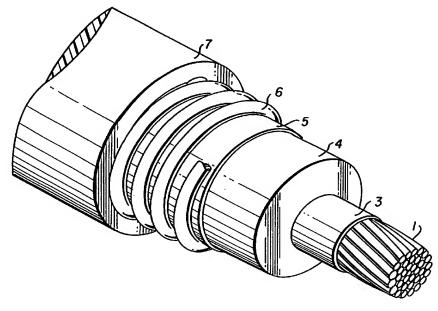
- (74) Agent: GREENBAUM, Michael, C.; Blank Rome Comisky & McCauley LLP, 900 17th Street, NW, Suite 1000, Washington, DC 20006 (US).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

with international search report

[Continued on next page]

(54) Title: LOW ADHESION SEMI-CONDUCTIVE ELECTRICAL SHIELDS



(57) **Abstract:** A low adhesion semiconductive dielectric shield for use with cross-linked polyethylene, ethylene-propylene-diene rubber (EPDM rubber) insulation. The dielectric shield comprises a base polymer which is a copolymer of ethylene with a monounsaturated ester; a conductive filler in an amount sufficient to give an electrical resistivity below 550 ohms-meter and as an adhesion adjusting device an ethylene vinyl acetate, ethylene alkyl methacrylate copolymer having a molecular weight above 20,000 daltons and a polydispersity greater than 2.5 wherein the adhesion between the insulation and the semiconductive shield is between about 3-26 lbs per 1/2 inch.



WO 02/31051 A1



 before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

LOW ADHESION SEMI-CONDUCTIVE ELECTRICAL SHIELDS

Field of Invention

The invention relates to polymer compositions and the use of these polymer compositions to manufacture semiconductive shields for use in electric cables, electric cables made from these compositions and methods of making electric cables from these compositions. More particularly, the invention relates to composition for use as strippable "semiconducting" dielectric shields (also referred to as the core shields, dielectric screen and core screen materials in power cables with cross linked polymeric insulation, primarily with medium voltage cables having a voltage from about 5 kV up to about 100kV.

Background of the Invention

In general, semiconducting dielectric shields can be classified into two distinct types, the first type being a type wherein the dielectric shield is securely bonded to the polymeric insulation so that stripping the dielectric shield is only possible by using a cutting tool that removes the dielectric shield along with some of the cable insulation. This type of dielectric shield is preferred by companies that believe that this adhesion minimizes the risk of electric breakdown at the interface of the shield and insulation. The second type of dielectric shield is the "strippable" dielectric shield wherein the dielectric shield has a defined, limited, adhesion to the insulation so that the strippable shield can be peeled cleanly away from the insulation without removing any insulation. Current strippable shield compositions for use over insulation selected from polyethylene, cross-linked polyethylenes, or one of the ethylene copolymer rubbers such as ethylene-propylene rubber (EPR) or ethylene-propylene diene terpolymer (EPDM) are usually based on an ethylene-vinyl acetate (EVA) copolymer base

resin rendered conductive with an appropriate type and amount of carbon black. The peel characterization of the strippable shield can be obtained by the proper selection of the EVA with a sufficient vinyl acetate content, usually about 32-40% vinyl acetate, and usually with a nitrile rubber as an adhesion-adjusting additive.

Strippable shield formulations of EVA and nitrile rubbers have been described by Ongchin, U.S. Patent Nos. 4,286,023 and 4,246,142; Burns et al. EP Application No. 0,420,271B, Kakizaki et al U. S. Patent No. 4,412,938 and Janssun, U.S. Patent No. 4,226,823, each reference being herein incorporated by reference into this application. A problem with these strippable shield formulations of EVA and nitrile rubber is that the EVA's needed for this formulation have a relatively high vinyl acetate content to achieve the desired adhesion level with the result that the formulations are more rubbery then is desired for high speed extrusion of a commercial electric cable.

Alternative adhesion-adjusting additives have also been proposed for use with EVA, for example waxy aliphatic hydrocarbons (Watanabe et al. U.S. Patent No. 4,933,107, herein incorporated by reference); low-molecular weight polyethylene (Burns Jr., U.S. Patent No. 4,150,193 herein incorporated by reference); silicone oils, rubbers and block copolymers that are liquid at room temperature (Taniguchi et al. U.S. Patent No. 4,493,787 herein incorporated by reference); chlorosulfonated polyethylene, ethylene-propylene rubbers, polychloroprene, styrene-butadiene rubber, natural rubber (all in Janssun) but the only one that appears to have found commercial acceptance was paraffin waxes.

Brief Description of the Figures

Fig. 1 is a cross-sectional representation of the electrical cable of the invention.

Fig. 2 is a perspective view of the electrical cable of the invention.

Brief Description of the Invention

This invention is based on the unexpected discovery that EVA waxes, ethylene alkyl acrylates or ethylene alkyl methacrylate copolymer waxes with a molecular weight greater than 20,000 and a polydispersity greater than 2 were good adhesion modifiers when used with a strippable semiconductive shield base resin and a conventional insulator. The strippable semiconductive shield base resin can include ethylene vinyl acetate copolymers, ethylene alkyl acrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons, ethylene alkyl methacrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons and ternary copolymers of ethylene with alkyl acrylates and alkyl methacrylates. The strippable semiconductive shield can include any suitable conductive carbon black in an amount to give the semiconductive shield an electrical resistance less than about 550 ohm-meter.

The invention includes electrical cables made using the strippable semiconductive shield of the invention as well as methods of making these electrical cables. The electrical cable of the invention include a conductive core surrounded by a semi-conductive layer that is surrounded by an insulating layer, the insulation of the insulating layer is selected from polyethylene, cross linked polyethylene (XLPE), ethylene-propylene rubbers and ethylene propylene diene rubbers (EPDM rubbers). The insulating layer is covered by the semiconductive dielectric shield of the invention and the semiconductive shield maybe covered by metal wires or strips that are then grounded upon installation of the cable and jacketing.

Detailed Description of the Invention

This invention includes strippable semiconductive shields suitable for use with conventional electrical insulators, electric power cables employing these strippable semiconductive dielectric shields and methods of making both the semiconductive shields and electric power cables employing these shields.

Conventional electrical insulators used in medium voltage cables include polyethylenes, cross-linked polyethylenes (XLPE), ethylene-propylene rubbers and ethylene propylene diene rubbers (EPDM rubbers). The term polyethylene is meant to include both polymers and copolymers wherein ethylene is the major component, this would include, for example, metallocene or single site catalyzed ethylenes that are copolymerized with higher olefins.

The strippable semiconductive shields of the invention comprise base resins, adhesion modifying compounds and conductive carbon blacks. The conductive carbon blacks are added in an amount sufficient to decrease the electrical resistivity to less than 550 ohmmeter. Preferably the resistivity of the semiconductive shield is less than about 250 ohmmeter and even more preferably less than about 100 ohmmeter.

The base resin is selected from any suitable member of the group consisting of ethylene vinyl acetate copolymers, ethylene alkyl acrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons, ethylene alkyl methacrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons and ternary copolymers of ethylene, alkyl acrylates and alkyl methacrylate wherein the alkyl group is independently selected from C1 to C6 hydrocarbons.

The ethylene vinyl acetate copolymer base resin can be any EVA copolymer with the

following properties: the ability to accept high loadings of conductive carbon filler, elongation of 150 to 250 percent and sufficient melt strength to maintain its shape after extrusion. EVA copolymers with vinyl acetate levels above about 25 percent and below about 45 percent having these properties are known. The EVA copolymers can have a vinyl acetate percentage range of about 25 to 45 percent. A preferred EVA copolymer will have a vinyl acetate percentage range of about 28 to 40 percent and an even more preferred EVA copolymer will have a vinyl acetate percentage of about 28 to 33 percent. The EVA copolymers can have a molecular weight from about 40,000 to 150,000 daltons preferably about 45,000 to 100,000 daltons and even more preferably about 50,000 to 75,000 daltons. Examples of suitable EVA copolymers would include Elvax® 150, Elvax® 240 and Elvax® 350, sold by DuPont Corp. of Wilmington Delaware.

The ethylene alkyl acrylate copolymers can be any suitable ethylene alkyl acrylate copolymers with the following properties: the ability to accept high loadings of conductive carbon filler, elongation of 150 to 250 percent and sufficient melt strength to maintain its shape after extrusion. The alkyl group can be any alkyl group selected from the C1 to C6 hydrocarbons, preferably the C1 to C4 hydrocarbons and even more preferable methyl. Some ethylene alkyl acrylate copolymers with alkyl acrylate levels above about 25 percent and below about 45 percent have these properties. The ethylene alkyl acrylate copolymers can have an alkyl acrylate percentage range of about 25 to 45 percent. A preferred ethylene alkyl acrylate copolymer will have an alkyl acrylate percentage range of about 28 to 40 percent and an even more preferred ethylene alkyl acrylate copolymer will have an alkyl acrylate percentage of about 28 to 33 percent. The ethylene alkyl acrylate copolymers can have a molecular weight from about 40,000 to 150,000 daltons preferably about 45,000 to 100,000

daltons and even more preferably about 50,000 to 75,000 daltons. An example would be Vamac® G or Vamac® HG sold by DuPont Corp. of Wilmington, Delaware.

The ethylene alkyl methacrylate copolymers can be any suitable ethylene alkyl methacrylate copolymer with the following properties: the ability to accept high loadings of conductive carbon filler, elongation of 150 to 250 percent and sufficient melt strength to maintain its shape after extrusion. The alkyl group can be any alkyl group selected from the C1 to C6 hydrocarbons, preferably the C1 to C4 hydrocarbons and even more preferable methyl. Some ethylene alkyl methacrylate copolymers with alkyl methacrylate levels above about 25 percent and below about 45 percent have these properties. The ethylene alkyl methacrylate copolymers can have an alkyl methacrylate percentage range of about 25 to 45 percent. A preferred ethylene alkyl methacrylate copolymer will have an alkyl methacrylate percentage range of about 28 to 40 percent and an even more preferred ethylene alkyl methacrylate copolymer will have an alkyl methacrylate percentage of about 28 to 33 percent. The ethylene alkyl methacrylate copolymers can have a molecular weight from about 40,000 to 150,000 daltons preferably about 45,000 to 100,000 daltons and even more preferably about 50,000 to 75,000 daltons. An example of a commercially available ethylene methyl methacrylate is 35MA05 from Atofina of Paris -La Defence, France.

The ternary copolymers of ethylene with alkyl acrylates and alkyl methacrylates can be any suitable ternary copolymer with the following properties: the ability to accept high loadings of conductive carbon filler, elongation of 150 to 250 percent and sufficient melt strength to maintain its shape after extrusion. The alkyl group can be any alkyl group independently selected from the C1 to C6 hydrocarbons, preferably the C1 to C4 hydrocarbons and even more preferable methyl. Usually a ternary copolymer will be

predominantly either an alkyl acrylate with a small portion of an alkyl methacrylate or an alkyl methacrylate with a small portion of an alkyl acrylate. The proportions of alkyl acrylate and alkyl methacrylate to ethylene will be about the same as the proportions described for ethylene alkyl acrylate copolymers or for ethylene alkyl methacrylate copolymers as well as the molecular weight ranges described for ethylene alkyl acrylate and ethylene alkyl methacrylate.

The adhesion modifying compounds are any suitable ethylene vinyl acetate copolymers with a molecular weight greater than about 20,000 daltons, a preferred ethylene vinyl acetate copolymer will have a molecular weight from about 22,500 to about 50,000 daltons and an even more preferred EVA copolymer will have a molecular weight from about 25,000 to about 40,000 daltons. The adhesion modifying ethylene vinyl acetate copolymers of the invention will have a polydispersivity greater than about 2.5 preferably a polydispersivity greater than 4 and even more preferably a polydispersivity greater than 5. Polydispersity is M_w divided by M_n and is a measure of the distribution of the molecular weights of the polymer chains. The proportion of vinyl acetate in the adhesion modifying ethylene vinyl acetate copolymers of the invention should be about 10 to 28 percent, preferably about 12 to 25 and even more preferably about 12 to 20 percent vinyl acetate. Suitable commercially available material includes AC 415, a 15 percent vinyl acetate wax available from Honeywell Inc. of Morristown, New Jersey.

The adhesion modifying compounds can also include any suitable ethylene alkyl acrylate or ethylene alkyl methacrylate copolymer wherein the alkyl group is selected from the C1 to C6 hydrocarbons and with a molecular weight greater than about 20,000 daltons, a preferred ethylene alkyl acrylate or ethylene alkyl methacrylate copolymer will have a

molecular weight from about 22,500 to about 50,000 daltons and an even more preferred ethylene alkyl acrylate or ethylene alkyl methacrylate copolymer will have a molecular weight from about 25,000 to about 40,000 daltons. The adhesion modifying ethylene alkyl acrylate or ethylene alkyl methacrylate copolymers of the invention will have a polydispersivity greater than about 2.5 preferably a polydispersivity greater than 4 and even more preferably a polydispersivity greater than 5. Polydispersity, as previously defined, is M_w divided by M_n and is a measure of the distribution of the molecular weights of the polymer chains. The proportion of alkyl acrylate or alkyl methacrylate in the adhesion modifying ethylene alkyl acrylate or ethylene alkyl methacrylate copolymers of the invention should be about 10 to 28 percent, preferably about 12 to 25 and even more preferably about 12 to 20 percent alkyl acrylate. The alkyl group is selected from the C1 to C6 hydrocarbons, preferably the C1 to C4 hydrocarbons and even more preferably methyl.

The conductive carbon black can be any conductive carbon blacks in an amount sufficient to decrease the electrical resistivity to less than 550 ohm-meter. Preferably the resistivity of the semiconductive shield is less than about 250 ohm-meter and even more preferably less than about 100 ohm-meter. Suitable carbon blacks include N351 carbon blacks and N550 carbon blacks sold by Cabot Corp. of Boston Mass.

The strippable semiconductive shield formulations of the invention can be compounded by a commercial mixer such as a Banbury mixer, a twin screw extruder a Buss Ko Neader or other continuous mixers. The proportion of the adhesion modifying compound to the other compounds in the strippable semiconductive shield will vary depending on the base polymer, underlying insulation, molecular weight of the adhesion modifying compound and polydispersity of the adhesion modifying compound. A strippable shield formulation can

be made by compounding 30 to 45 percent by weight carbon black with 0.5 to 10 percent by weight adhesion modifying compound, and the balance the base polymer, optionally any one of, the following components may be added 0.05 to 3.0 percent by weight process aid, 0.05 to 3.0 percent by weight antioxident, 0.1 to 3.0 percent by weight cross-linking agent. Another strippable shield formulation can have 33 to 42 percent by weight carbon black, 1.0 to 7.5 weight percent adhesion modifying compound and the balance base polymer optionally any one of, the following components may be added: 0.1 to 2.0 percent by weight process aid, 0.1 to 2.0 percent by weight antioxident, 0.5 to 2.0 percent by weight cross-linking agent. Still another strippable shield formulation can have 35 to 40 percent by weight carbon black, 2.0 to 7.0 percent by weight adhesion modifying compound, and the balance base polymer optionally any one of, the following components may be added: 0.25 to 1.5 percent by weight process aid, 0.25 to 1.5 percent by weight antioxident, 1.0 to 2.0 percent by weight crosslinking agent. The strippable shield formulation can be compounded by mixing the carbon black, adhesion modifying compound, processing aid, anti-oxident and base polymer together in a continuous mixer until well mixed and then the cross linking agent may be added in a second mixing step or absorbed into the polymer mass after mixing. After addition of the cross-linking agent the formulation is ready to be extruded onto the insulation and crosslinked to form the strippable semiconductive shield.

The cross linking agent can be chosen from any of the well know cross-linking agents known in the art including silanes that are cross-linked by moisture and peroxides that form free radicals and cross-link by a free radical mechanism.

The invention includes electrical cables made using the strippable semiconductive shield of the invention as well as methods of making these electrical cables. As seen in

Figures 1 and 2, the electrical cable of the invention includes a conductive core (1) surrounded by a semi-conductive layer (3) that is surrounded by an insulating layer (4), the insulation of the insulating layer is selected from polyethylene, cross linked polyethylene (XLPE), ethylene-propylene rubbers and ethylene propylene diene rubbers (EPDM rubbers). The insulating layer (4) is covered by the semiconductive dielectric shield (5) of the invention and the semiconductive shield maybe covered by metal wires or strips (6) that are then grounded upon installation of the cable and jacketing (7).

The electrical cable of the invention can be made by any of the methods well known in the art including coating a metal conductor with a semi-conductive layer and in a double extrusion crosshead extruding the insulating layer and the strippable semi-conductive shield together in a simultaneous extrusion or simultaneously extruding a semiconductive layer around a metal conductor, an insulating layer around the semiconductive layer and a strippable semiconductive shield around the insulating layer by using a triple extrusion crosshead. The semiconductive shield, insulating layer and strippable semiconductive shield may then be allowed to internally cross-link if desired. Metal wires or strips are then wrapped around the cable and a jacket is placed over the metal wire or strips to form a finished cable.

Examples

The compositions tabulated below were made up by the procedure set out after the table, and made up into moulded plaques measuring 150 mm square by 2mm thick, one face being plaques measuring 150 mm square by 2mm thick, one face being bonded to an XLPE block of the same dimensions and the two compositions cured together in the press for 20

min at 180°C. Selected compositions only were made up in large quantities by a similar procedure in a Buss Ko Neader continuous compounding extruder and dual-extruded under standard commercial conditions for the respective materials onto sample cables with either XLPE or EPR insulation having an external diameter of 20 mm to form a dielectric screen 1.0 mm thick. In each case adhesion was measured by the peel strength tests detailed below. Identification of ingredients also follows after the Table. In the table, numbered Examples are in accordance with the invention; lettered Examples are for comparison. Each Example was also formulated with 0.8 weight percent processing aid (zinc stearate), 0.5 weight percent anti-oxidant (polymerized 1,2 dihydro -2, 2, 4 trimethyl quinoline, Agerite MA, from R.T. Vanderbilt) and 1.5 weight percent cross-linking agent (tert-butyl cumyl peroxide).

Table 1: EVA with 40% Vinyl Acetate

Example	A	В	1	. 2	3	4	5	6	7
Base	EVA 40	EVA 40	EVA 40	EVA 40	EVA 40	EVA 40	EVA 40	EVA 40	EVA 40
Polymer									
(Parts)	60.5	56.7	56.7	56.7	56.7	59.7	58.7	60.7	57.7
Adhesion	·	AC	AMC ²						
Modifier		400	67	67	70	91	91	67	67
(% Vinyl		(13%)	(16%)	(16%)	(20%)	(13%)	(13%)	(14%)	(14%)
Acetate)									
Parts	_	(5)	(5)	. (5)	(5)	(2)	(3)	(1)	(4)
Adhesion	12.0	9.9	8	6.5	6.5	7.1	7	8.7	1.8

^{1.} The MW of Ac400 is less than 20,000 Daltons.

^{2.} AMC stands for "adhesion modifying compound" and these compounds are ethylene vinyl acetate waxes with the vinyl acetate content indicated with a range of molecular weights greater than 20.000 daltons and with

a range of polydispersivitys greater than 2.5

Table 2: EVA with 32% Vinyl Acetate

Example	C	D	Е	6	7	8	9	10	11
Base	EVA 32	EVA 32	EVA 32	EVA 32	EVA 32	EVA 32	EVA 40	EVA	EVA
Polymer								56.7	57.7
(Parts)	60.3	56.7	56.7	56.7	56.7	56.7	58.7	56.7	57.7
Adhesion	_	AC	AC 400 ¹	AMC ²					
Modifier		4001	(13%)	66	67	68	69	70	37
(% Vinyl		(13%)		(12%)	(14%)	(16%)	(18%)	(20%)	(14%)
Acetate)									
Parts		(5)	(5)	(5)	(5)	(2)	(3)	(1)	(4)
					ı				
Carbon	N 351	N 351	N 550	N 351	N 351	N 381	N 351	N 351	N 351
Туре									
Parts	37	37	37	. 37	37	37	37	37	37
Adhesion	19	12-13.3	8.9	11.1	7.7	7.9	8.2	9.9	8.1

^{1.} The MW of Ac400 is less than 20,000 Daltons.

2. AMC stands for "adhesion modifying compound" and these compounds are ethylene vinyl acetate waxes with the vinyl acetate content indicated with a range of molecular weights greater than 20.000 daltons and with a range of polydispersivitys greater than 2.5.

Table 3: EVA with 28% Vinyl Acetate

Example	F	G	Н	12	13
Base Polymer	EVA 28				
(Parts)	60.3	56.7	58.75	56.7	56.7

Adhesion Modifier		AC 4001	AC 415 ³	AMC ² 67	AMX ² 69
(% Vinyl Acetate)		(13%)		(14%)	(16%)
Parts		5	3	5	5
Carbon Type	N 315	N 351	N 351	N 351	N 550
Parts	37	37	37	37	37
Adhesion	30	14	13.2	11.3	10.0

- 1. The MW of Ac400 is less than 20,000 Daltons and the polydispersity is less than 2.
- 2. AMC stands for "adhesion modifying compound" and these compounds are ethylene vinyl acetate waxes with the vinyl acetate content indicated with a range of molecular weights greater than 20.000 daltons and with a range of polydispersivitys greater than 2.5.
- 3. The MW of AC415 is greater than 20,000 and the polydispersivity is greater than 2.5.

Table 4 EVA with a Vinyl Acetate content of 25%

Example	I	J	14	15	16
Base Polymer	EVA 25	EVA 25	EVA 25	EVA 25	EVA 25
(Parts)	60.2	56.7	56.7	56.7	56.7
Adhesion Modifier	. —	AC 4001	AMC ² 66	AMC ² 68	AMC ²
(% Vinyl Acetate)	e)	(13%)	(12%)	(5%)	70 (20%)
Parts		5	2	3	1
Carbon Type	N 351	N 550	N 550	N 550	N 550
Parts	37	37	37	37	37
Adhesion	Bonded	15.1	19.	11.8	15.5

- 1. The MW of Ac400 is less than 20,000 Daltons and the polydispersity is less than 2.
- 2.AMC stands for "adhesion modifying compound" and these compounds are ethylene vinyl acetate waxes with

the vinyl acetate content indicated with a range of molecular weights greater than 20.000 daltons and with a range of polydispersivitys greater than 2.5.

Example	К	17	18
Base Polymer	EVA34	EVA32	EVA32
(Parts)	56.7	56.7	56.7
Adhesion Modifer (% Vinyl Acetate)	AC 400 ¹ (13%)	AC 415 ² (14-16%) Sample 1	AC 415 ² (14-16%) Sample 2
Parts	5	5	5
Carbon Type	N351	N 351	N 351
Parts	37	37	37
Adhesion on Plaque	12	10	11
Adhesion on Cable	14-18 lb	9-10	12-14

- 1. The MW of Ac400 is less than 20,000 Daltons and the polydispersity is less than 2.
- 2. The MW of AC415 is greater than 20,000 and the polydispersivity is greater than 2.5.

Mixing Procedure

Banbury mixer with a capacity of 1.57 1. Half the base polymer and half the adhesion-adjusting additive were first introduced into the cold Banbury and fluxed at its middle speed setting; the processing aid and antioxidant were added together, followed immediately by the carbon black. The ram was lowered and raised and the remainder of the base polymer and adhesion-adjusting additive were added and blending continued until the temperature reached 135°C (275°F). The material was discharged and cooled to ambient temperature, and then half of it reintroduced to the cold Banbury, fluxed and the peroxide added, followed immediately by the remainder of the mixture, blending was continued until the temperature reached 110°C (230°F) and the mixture discharged and promptly moulded.

Ingredients:

EVA 34: ethylene-vinyl acetate copolymer, 34% vinyl acetate content, 43 melt index, sold under the trademark ELVAX as Elvax EP4174 by the Dupont Corp.

EVA 32: ethylene-vinyl acetate copolymer, 32% vinyl acetate content, 43 melt index, sold under the Trademark ELVAX as Elvax 150 by the Dupont Corp.

EVA 40: ethylene-vinyl acetate copolymer, 40%vinyl acetate content, 57 melt index, sold under the trademark ELVAX as Elvax 40W by the Dupont Corp.

EVA 28: ethylene-vinyl acetate copolymer, 28% vinyl acetate content, 43 melt index, sold under the trademark Elvax as Elvax 240 by the Dupont Corp.

EVA 25: ethylene-vinyl acetate copolymer, 25% vinyl acetate content, 19 melt index, sold under the trademark Elvax as Elvax 350 by the Dupont Corp.

AC400: ethylene-vinyl acetate copolymer of molecular weight about 17,934 Daltons, 13% vinyl acetate content, polydispensivity of 1.9, 92°C (198°F) Mettler drop point, sold by Allied Signal under this designation.

AC 415 is an ethylene vinyl acetate wax with 14-16 percent vinyl acetate, a molecular weight of 22,500 - 50,000 daltons and a polydispersivity of 2.5-10.

AMC stands for "adhesion modifying compound" and these compounds are various experimental EVA waxes with the vinyl acetate composition indicated in the tables and a range of molecular weights greater than 20,000 daltons and with a range of polydispersivitys greater than 2.5.

N351 carbon black and N550 carbon black are conductive carbon blacks obtained from Cabot Corp. of Boston Mass.

Adhesion tests

Plaque samples were tested by cutting completely through the thickness of the layer of the experimental shield composition in parallel lines to define a strip 12.5m (½ inch) wide; one end was lifted and turned back 180° to lie along the surface of the portion still adhered, and the force required to peel at a rate of 0.0085m/s (20in/min) measured; peel strength was calculated in N/m and pounds per ½ inch.

Cable samples were tested generally in the same way, with the cuts parallel to the cable axis, but the peeling force was applied an measured in a direction at 90° to the surface, instead of 180°. Because of the different preparation and crosslinking methods used in preparing plaques compared to extruding cable as well as this difference in pulling direction, plaque and cable peel strengths are not directly comparable but plaque tests do provide a useful guide in the development process: typically cable peel force is measured at a 90 degree angle with the cable will prove to be roughly twice the plaque peel force which is measured at a 180 degree angle which is also called "T peel."

Claims

1. A strippable semiconductive shield comprising,

a base polymer selected from the group consisting of ethylene vinyl acetate copolymers, ethylene alkyl acrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons, ethylene alkyl methacrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons and ethylene alkyl acrylate alkyl methacrylate terpolymers wherein the alkyl group is independently selected from C1 to C6 hydrocarbons;

an adhesion modifying compound comprising an ethylene vinyl acetate with a molecular weight greater than about 20,000 daltons and a polydispersivity greater than about 2.5;

a conductive carbon black in an amount sufficient to give the semiconductive shield a resistance below about 550 ohm-meter.

- 2. The strippable semiconductive shield of claim 1 wherein the base polymer is ethylene vinyl acetate copolymers.
- 3. The strippable semiconductive shield of claim 1 wherein the base polymer is ethylene alkyl acrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons.
- 4. The strippable semiconductive shield of claim 1 wherein the base polymer is ethylene alkyl methacrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons.

5. The strippable semiconductive shield of claim 1 wherein the base polymer is ethylene alkyl acrylate alkyl methacrylate terpolymers wherein the alkyl group is independently selected from C1 to C6 hydrocarbons.

- 6. The strippable semiconductive shield of claim 1 wherein the adhesion modifying compound comprises an ethylene vinyl acetate with a molecular weight from about 22,500 to about 50,000 daltons.
- 7. The strippable semiconductive shield of claim 6 wherein the adhesion modifying ethylene vinyl acetate has a molecular weight from about 25,000 to about 40,000 daltons.
- 8. The strippable semiconductive shield of claim 1 wherein the adhesion modifying compound comprises an ethylene vinyl acetate with a polydispersivity greater than 4.
- 9. The strippable semiconductive shield of claim 1 wherein the adhesion modifying compound comprises an ethylene vinyl acetate with a polydispersivity greater than 5.
- 10. The strippable semiconductive shield of claim 1 wherein the adhesion modifying compound comprises an ethylene vinyl acetate having a vinyl acetate composition between about 10 to 28 percent.
- 11. The strippable semiconductive shield of claim 10 wherein the adhesion modifying ethylene vinyl acetate has a vinyl acetate composition between about 12 to 25 percent.

12. The strippable semiconductive shield of claim 1 wherein the carbon black is selected from N550 and N351 type carbon blacks.

- 13. The strippable semiconductive shield of claim 1 wherein the semiconductive shield further includes a cross-linking agent.
- 14. The strippable semiconductive shield of claim 1 wherein the semiconductive shield comprises 30 to 45 percent by weight carbon black and 0.5 to 10 percent by weight adhesion modifier.
- 15. The strippable semiconductive shield of claim 1 wherein the semiconductive shield comprises 33 to 42 percent by weight carbon black and 1.0 to 7.5 weight percent adhesion modifying compound.
- 16. A method of making a strippable semiconductive shield comprising the steps of compounding a base polymer selected from the group consisting of ethylene vinyl acetate copolymers, ethylene alkyl acrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons, ethylene alkyl methacrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons and ethylene alkyl acrylate alkyl methacrylate terpolymers wherein the alkyl group is independently selected from C1 to C6 hydrocarbons with;

an adhesion modifying compound comprising an ethylene vinyl acetate with a molecular weight greater than about 20,000 daltons and a polydispersivity greater than about

2.5 and

a conductive carbon black in an amount sufficient to give the semiconductive shield a resistance below about 550 ohm-meter together in a mixer to form a mixture and extruding the mixture to form the strippable semiconductive shield.

- 17. The method of claim 16 further comprising the step of adding a cross-linking agent to the mixture.
- 18. The method of claim 17 further comprising the step of cross-linking the strippable semiconductive shield.
- 19. The method of claim 16 wherein the strippable semiconductive shield comprises 30 to 45 weight percent carbon black and 0.5 to 10 weight percent adhesion modifier.
- 20. The method of claim 16 wherein the strippable semiconductive shield comprises 33 to 42 weight percent carbon black and 1.0 to 7.5 weight percent adhesion modifier.
- 21. A medium voltage electric power cable comprising a conductive core, and insulating layer, a strippable semiconductive shield, a grounded metal wire or tape and a jacket; wherein said strippable semi-conductive shield comprises,

a base polymer selected from the group consisting of ethylene vinyl acetate copolymers, ethylene alkyl acrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons, ethylene alkyl methacrylate copolymers wherein the alkyl group is

selected from C1 to C6 hydrocarbons and ethylene alkyl acrylate alkyl methacrylate terpolymers wherein the alkyl group is independently selected from C1 to C6 hydrocarbons;

an adhesion modifying compound comprising an ethylene vinyl acetate with a molecular weight greater than about 20,000 daltons and a polydispersivity greater than about 2.5;

a conductive carbon black in an amount sufficient to give the semiconductive shield a resistance below about 550 ohm-meter.

- 22. The power cable of claim 21 wherein the base polymer is ethylene vinyl acetate copolymers.
- 23. The power cable of claim 21 wherein the base polymer is ethylene alkyl acrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons.
- 24. The power cable of claim 21 wherein the base polymer is ethylene alkyl methacrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons.
- 25. The power cable of claim 21 wherein the base polymer is ethylene alkyl acrylate alkyl methacrylate terpolymers wherein the alkyl group is independently selected from C1 to C6 hydrocarbons.
- 26. The power cable of claim 21 wherein the adhesion modifying compound comprises an ethylene vinyl acetate with a molecular weight from about 22,500 to about 50,000 daltons.

27. The power cable of claim 26 wherein the ethylene vinyl acetate has a molecular weight greater than about 25,000 to about 40,000 daltons.

- 28. The power cable of claim 21 wherein the adhesion modifying compound comprises an ethylene vinyl acetate with a polydispersivity greater than 4.
- 29. The power cable of claim 21 wherein the adhesion modifying compound comprises an ethylene vinyl acetate with a polydispersivity greater than 5.
- 30. The power cable of claim 21 wherein the adhesion modifying compound comprises an ethylene vinyl acetate having a vinyl acetate composition between about 10 to 28 percent.
- 31. The power cable of claim 30 wherein the ethylene vinyl acetate has a vinyl acetate composition between about 12 to 25 percent.
- 32. The power cable of claim 21 wherein the carbon black is selected from N550 and N351 type carbon blacks.
- 33. A method of making a medium voltage electric power cable having a strippable semiconductive shield comprising the steps of simultaneously extruding through a triple extrusion crosshead a semiconductive layer encasing a metal conductor, an insulating layer encasing the semiconductive layer and a strippable semiconductive layer encasing the insulating layer, wrapping the strippable semiconductive layer with metal wire or metal strips

and placing a jacket over the metal wire or strips, wherein said strippable semiconductive comprises

a base polymer selected from the group consisting of ethylene vinyl acetate copolymers, ethylene alkyl acrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons, ethylene alkyl methacrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons and ethylene alkyl acrylate alkyl methacrylate terpolymers wherein the alkyl group is independently selected from C1 to C6 hydrocarbons;

an adhesion modifying compound comprising an ethylene vinyl acetate with a molecular weight greater than about 20,000 daltons and a polydispersivity greater than about 2.5;

a conductive carbon black in an amount sufficient to give the semiconductive shield a resistance below about 550 ohm-meter.

- 34. The method of claim 33 wherein the insulating layer is cross-linked after extrusion.
- 35. The method of claim 34 wherein the semiconductive shield is cross-linked after extrusion.
- 36. A method of making a medium voltage electric power cable having a strippable semiconductive shield comprising the steps of simultaneously extruding through a double extrusion crosshead onto a semiconductive layer encasing a metal conductor, an insulating layer encasing the semiconductive layer and a strippable semiconductive layer encasing the insulating layer, wrapping the strippable semiconductive layer with metal wire or metal strips

and placing a jacket over the metal wire or strips, wherein said strippable semiconductive comprises

a base polymer selected from the group consisting of ethylene vinyl acetate copolymers, ethylene alkyl acrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons, ethylene alkyl methacrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons and ethylene alkyl acrylate alkyl methacrylate terpolymers wherein the alkyl group is independently selected from C1 to C6 hydrocarbons;

an adhesion modifying compound comprising an ethylene vinyl acetate with a molecular weight greater than about 20,000 daltons and a polydispersivity greater than about 2.5;

a conductive carbon black in an amount sufficient to give the semiconductive shield a resistance below about 550 ohm-meter.

- 37. The method of claim 36 wherein the insulating layer is cross-linked after extrusion.
- 38. The method of claim 36 wherein the semiconductive shield is cross-linked after extrusion.
- 39. A strippable semiconductive shield comprising,

a base polymer selected from the group consisting of ethylene vinyl acetate copolymers, ethylene alkyl acrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons, ethylene alkyl methacrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons and ethylene alkyl acrylate alkyl methacrylate

terpolymers wherein the alkyl group is independently selected from C1 to C6 hydrocarbons;

an adhesion modifying compound comprising a member of the group selected from an ethylene alkyl acrylate and an ethylene alkyl methacrylate copolymer wherein the alkyl group is selected from the C1 to C6 hydrocarbons and with a molecular weight greater than about 20,000 daltons and a polydispersivity greater than about 2.5;

a conductive carbon black in an amount sufficient to give the semiconductive shield a resistance below about 550 ohm-meter.

- 40. The strippable semiconductive shield of claim 29 wherein the base polymer is ethylene vinyl acetate copolymers.
- 41. The strippable semiconductive shield of claim 39 wherein the base polymer is ethylene alkyl acrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons.
- 42. The strippable semiconductive shield of claim 39 wherein the base polymer is ethylene alkyl methacrylate copolymers wherein the alkyl group is selected from C1 to C6 hydrocarbons.
- 43. The strippable semiconductive shield of claim 39 wherein the base polymer is ethylene alkyl acrylate alkyl methacrylate terpolymers wherein the alkyl group is independently selected from C1 to C6 hydrocarbons.

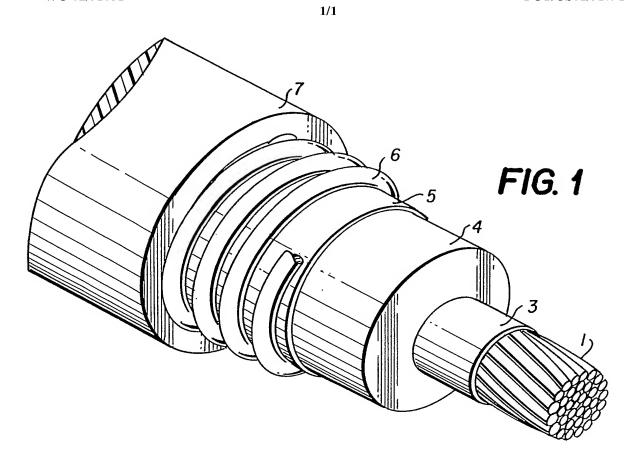
44. The strippable semiconductive shield of claim 39 wherein the adhesion modifying compound comprises an ethylene alkyl acrylate copolymer with a molecular weight from about 22,500 to about 50,000 daltons.

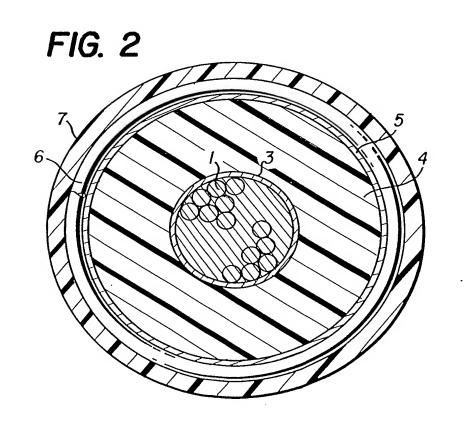
- 45. The strippable semiconductive shield of claim 44 wherein the ethylene alkyl acrylate has a molecular weight from about 25,000 to about 40,000 daltons.
- 46. The strippable semiconductive shield of claim 39 wherein the adhesion modifying compound comprises an ethylene alkyl acrylate or ethylene alkyl methacrylate with a polydispersivity greater than 4.
- 47. The strippable semiconductive shield of claim 39 wherein the adhesion modifying compound comprises an ethylene alkyl acrylate or ethylene alkyl methacrylate with a polydispersivity greater than 5.
- 48. The strippable semiconductive shield of claim 39 wherein the carbon black is selected from N550 and N351 type carbon blacks.
- 49. The strippable semiconductive shield of claim 39 wherein the semiconductive shield further includes a cross-linking agent.
- 50. The strippable semiconductive shield of claim 39 wherein the semiconductive shield comprises 30 to 45 percent by weight carbon black and 0.5 to 10 percent by weight adhesion

modifier.

51. The strippable semiconductive shield of claim 39 wherein the semiconductive shield comprises 33 to 42 percent by weight carbon black and 1.0 to 7.5 weight percent adhesion modifying compound.

- 52. The strippable semiconductive shield of claim 39 wherein the adhesion modifying compound comprises an ethylene alkyl methacrylate copolymer with a molecular weight from about 22,500 to about 50,000 daltons.
- 53. The strippable semiconductive shield of claim 52 wherein the ethylene alkyl acrylate has a molecular weight from about 25,000 to about 40,000 daltons.





INTERNATIONAL SEARCH REPORT

Inte al Application No PC 1/US 01/31791

Relevant to claim No.

1,2

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Category °

Χ

 $\begin{array}{ll} \mbox{Minimum documentation searched (classification system followed by classification symbols)} \\ \mbox{IPC 7} & \mbox{C08L} & \mbox{C08K} & \mbox{H01B} \end{array}$

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

Citation of document, with indication, where appropriate, of the relevant passages

WO 98 21278 A (BICC PLC ; EASTER MARK

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

	RICHARD (US)) 22 May 1998 (1998-		± , £
Y	example C page 3, line 24 —page 5, line 17 1—25	; claims	3-53
Х	US 6 013 202 A (KEEN FIONA ELEAN 11 January 2000 (2000-01-11) examples 1,2	NOR ET AL)	1,2
Y	column 3, line 33 -column 5, lir claims 1-20	ne 23;	3–53
х	US 4 286 023 A (ONGCHIN LUCIO) 25 August 1981 (1981-08-25) column 2, line 15 -column 4, lir claims 1-11	ne 49;	1,2
		_/	
X Furth	ner documents are listed in the continuation of box C.	χ Patent family members are listed	in annex.
"A" docume consid "E" earlier or filing d "L" docume which in citation "O" docume other n	nt which may throw doubts on priority claim(s) or is cited to establish the publication date of another n or other special reason (as specified) ent referring to an oral disclosure, use, exhibition or	 "T" later document published after the inte or priority date and not in conflict with cited to understand the principle or thinvention "X" document of particular relevance; the cannot be considered novel or cannot involve an inventive step when the document of particular relevance; the cannot be considered to involve an indocument is combined with one or moments, such combined with one or moments, such combination being obvious in the art. "&" document member of the same patent 	eary underlying the claimed Invention be considered to current is taken alone claimed invention claimed invention claimed invention claimed invention claimed invention claim
Date of the a	actual completion of the international search	Date of mailing of the international sea	arch report
1:	1 March 2002	18/03/2002	
Name and n	nailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Wengeler, H	
Form PCT/ISA/2	210 (second sheet) (July 1992)		

INTERNATIONAL SEARCH REPORT

Internal Application No PC 1/ U.S. 01/31791

		PC1/03 01/31/91
	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 334 992 A (HITACHI CABLE) 4 October 1989 (1989-10-04) examples 7,8,10	1,2
Y	EP 0 334 992 A (HITACHI CABLE) 4 October 1989 (1989-10-04) examples 7,8,10 page 3, line 30 -page 4, line 41; claims 1-16	1,2

INTERNATIONAL SEARCH REPORT

Interi al Application No
PCI/US 01/31791

Patent document cited in search repor	t	Publication date		Patent family member(s)	Publication date
WO 9821278	Α	22-05-1998	AU WO	4956097 A 9821278 A1	03-06-1998 22-05-1998
US 6013202	A	11-01-2000	NONE		
US 4286023	A	25-08-1981	US CA	4246142 A 1100306 A1	20-01-1981 05-05-1981
EP 0334992	А	04-10-1989	JP JP JP CA DE DE US	1246708 A 1860495 C 5077123 B 1317050 A1 3852541 D1 3852541 T2 0334992 A1 4933107 A	02-10-1989 27-07-1994 26-10-1993 27-04-1993 02-02-1995 04-05-1995 04-10-1989 12-06-1990